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(54) POROUS FILM, PREPARATION OF THE SAME, RECORDING MATERIAL USING SAID POROUS FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a porous film which is useful as a recording material capable of offering a print having excellent sharpness and having good handleability and, in addition, is utilizable in various fields, and to provide a process for preparing the same and use thereof.

SOLUTION: This porous film having a number of micropores created by gaps among particles is prep'd. by agglomerating polymer particles in an emulsion while maintaining the particulate form to form a film. The process for preparing the porous film comprises the steps of: forming a layer comprising at least an emulsion; unstabilizing the emulsion before water is entirely scattered from the layer, thereby agglomerating polymer particles in the emulsion, and then conducting drying.

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CLAIMS

[Claim(s)]

[Claim 1] Porous membrane characterized by forming much micropores by the gap of particles by making the polymer particle in an emulsion condense with the particle condition maintained, and making it coat-size.

[Claim 2] Porous membrane characterized by including a polymer particle and a gelling agent.

[Claim 3] Condensation of a polymer particle is porous membrane according to claim 1 which is what is performed by destabilizing an emulsion.

[Claim 4] Destabilization of an emulsion is porous membrane according to claim 3 which is what is performed with the sensible-heat gelling agent which can destabilize an emulsion with heating.

[Claim 5] Porous membrane according to claim 1 to 4 whose mean particle diameter of a polymer particle is 10 micrometers or less.

[Claim 6] Porous membrane according to claim 1 to 5 which is what has many holes with an average diameter of 500nm or less.

[Claim 7] The manufacture approach of the porous membrane characterized by being the approach of manufacturing porous membrane according to claim 1 to 6, destabilizing an emulsion, making the polymer particle in an emulsion condense before all water disperses from this layer, after forming the layer which contains an emulsion at least, and subsequently making it dry.

[Claim 8] The recorded material characterized by using the porous membrane indicated by either of claims 1-7 as an ink acceptance layer.

[Claim 9] The recorded material according to claim 8 which is what is used for an ink jet recording method.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention makes a detail coat-ize the polymer particle in an emulsion about the polymer coat which has many detailed and uniform holes with a diameter of 500nm or less, its process, and operation, maintaining the particle condition mostly, and relates to the completely new porous membrane which might make the gap of a polymer particle and a particle remain as puncturing. Although the porous membrane of this invention is available for various applications, it is useful especially as a recorded material. Therefore, although the content of this invention is targetted the recorded material field in the following explanation, of course, it is not that the application of the porous membrane of this invention is limited to a recorded material.

[0002]

[Description of the Prior Art] An ink jet recording method is made into a globule, and disperses ink, and it is the approach of making this adhere to a recorded material and recording it, there is little noise, and it is a high speed, and is used abundantly as an approach that multicolor printing can also be performed vividly. Recently, also close [the man in the street], the printer of an ink jet recording method etc. exists especially with the spread of color printers.

[0003] By the way, by the ink jet recording method, water color ink is mainly used in respect of the printing engine performance or an environmental problem. However, the film for over head projectors (OHP) used at a board, an institute, an examination meeting, etc. was a polyethylene terephthalate (PET) raw material, since the hydrophilic property was low, the water color ink of an ink jet recording method crawled, or it bled, or it carried out, and there was a problem of the ability not to make it established vividly.

[0004] For this reason, examination which enables it to print the manuscript of OHP by the printer of an ink jet method is made by forming the ink acceptance layer which can be received and established in water ink for the raw material of a hydrophilic property on a PET film. For example, although invention which prepares the porous layer containing the resin for binding, an organic particle with a mean particle diameter of 0.1-3 micrometers, and/or a restoration particle called colloidal silica in JP,57-14091,A was indicated, in the result which this invention person etc. retested, it was difficult to decide the amount of optimal mixing of the resin for binding, and a particle, and it was a thing inferior to the transparency of a porous layer. moreover, if there are too many amounts of resin, fixable [of ink] will obtain -- not having -- reverse -- the amount of resin -- being few (there being many amounts of particles) -- since a particle separated from a base material front face, and it fell or a particle condensed secondarily, there was also a problem of being inferior to the resolution of the printed image.

[0005] The sheet for record which prepares the porous layer to which the particle thickness of a direction vertical to a field (010) becomes JP,5-32414,A from the pseudo-boehmite of the floc of the boehmite crystal whose spacing of a field (020) is 6.17A or less by 70A or more on the other hand on a PET base material is indicated. Current marketing of the sheet obtained by this invention was carried out, although fixable [of ink] was good, a fingerprint tended to be attached and there were the offensive odor by the acetic acid used during [other than the

inconvenience on handling of discoloring if gas is adsorbed] manufacture remaining, and a problem that transparency was inferior a little. Although it is solvable by making detailed particle size of the pseudo-boehmite of a porous layer, since surface activity will go up too much, will condense and will be troubled by handling if a non-subtlety particle is made detailed, transparency is considered that solution is difficult. Furthermore, the opinion that this sheet is very expensive (4 or more times of the usual OHP) is also going up from the consuming public. [0006] For this reason, the film which coated the PET film with the water-soluble polymer more for the purpose of offer of the OHP film for ink jets of a low price is marketed. However, in order to use a water-soluble polymer as an ink acceptance layer, this commercial item was weak to humidity, and if not packed with a damp-proof film, it had the problem that an ink acceptance layer will dissolve and exfoliate blocking after a lifting and printing if moisture adheres to a sheet.

[0007]

[Problem(s) to be Solved by the Invention] So, in this invention, the clear image could be printed, and it excelled in the repeatability of an image and a color, or color enhancement, and hung up as a technical problem offering the recorded material which moreover does not have the inconvenience on handling, and offering available porous membrane, and its manufacture approach and operation also in further various fields.

[0008]

[Means for Solving the Problem] This invention has a summary at the porous membrane in which much micropores by the gap of particles were formed, and the made place by making the polymer particle in an emulsion condense with the particle condition maintained, and making it coat-ize. As for condensation of a polymer particle, in this invention, it is desirable to carry out by destabilizing an emulsion. Since there is a method of using a gelling agent as one in the approach of destabilizing an emulsion, the porous membrane which consists of the polymer particle and gelling agent in an emulsion is also contained in this invention. As a gelling agent, utilization of the sensible-heat gelling agent which can destabilize an emulsion with heating is simple, and desirable.

[0009] In this invention, it is desirable that the mean particle diameter of the polymer particle in an emulsion is 10 micrometers or less transparency and in respect of color enhancement, and since the gap of such particles is punctured, an average diameter can obtain the porous membrane to which much micropores 500nm or less exist in the film.

[0010] In order to manufacture the porous membrane of this invention, after forming the layer which contains an emulsion at least, it is good to adopt the approach of making destabilize an emulsion, making condense the polymer particle in an emulsion, before all water disperses from this layer, and subsequently drying. Although the porous membrane of this invention has various utility value, it is suitable to use it as an ink acceptance layer of a recorded material especially, and the activity as a recorded material for ink jet recording methods is recommended especially.

[0011]

[Embodiment of the Invention] The porous membrane of this invention makes the polymer particle in an emulsion condense with the particle condition maintained, and has the greatest point at the place made to coat-ize. The difference when coat-izing a general emulsion is explained like the formation fault of the porous membrane of this invention using drawing. It is drawing in which A of drawing 1 showed the coat-ized device of the usual emulsion, and B and C showed the molding machine style of the porous membrane of this invention in model. The usual emulsion is (1). After forming an emulsion layer by carrying out coating of the emulsion, since water exists enough in this layer, in early stages of the desiccation phase, it is moving about the polymer particle freely by Brownian motion.

(2) If desiccation progresses and the amount of water decreases considerably, with the surface tension of water, a particle can be mutually drawn near and will be in a closest packing condition.

(3) By the capillary pressure of extant water, that a polymer chain (segment) exercises and carries out counter diffusion, or the viscous flow of a polymer chain, while a particle deforms, weld the particle which changed into the closest packing condition.

(4) A particle interface disappears and a uniform continuation coat is formed. It coat-izes by the device to say.

[0012] On the other hand, it sets to the pattern of B and the porous membrane of this invention is (1). It is the same as A.

(2) Holding the particle shape by destabilizing an emulsion in the phase where water still exists enough in an emulsion layer, as for a polymer particle, gel, and condense and a particle joins together in the condition with a gap.

(3) With the condition that a particle has a gap and joined together, when water disperses, porous membrane is formed. It is (1) and (2) so that it may say and may be shown as C. It is the same as B.

[0013] (3) (2) Although it sets, and a particle has a gap and joins together, it welds to the particle by which a part of particle adjoins at the time of stoving. However, since it is slight deformation and welding which is extent in which the opening between particles remains, porous membrane is formed too. It says.

[0014] In addition, since a part of particle carries out deformation weld of the case of this C pattern, the physical reinforcement as film becomes good rather than the pattern of B in many cases. In the porous membrane of the pattern of B, a particles bridge formation system may be used in order to ensure association of a particle and a particle and to form strong porous membrane.

[0015] Thus, in this invention, since it condenses, maintaining that particle condition mostly before water disperses (the pattern of Above B and the pattern of C are set and it expresses hereafter, saying, "the particle condition was maintained mostly"), particles join together in the condition with a gap, and the polymer particle in an emulsion is coat-ized, when water disperses after that. For this reason, the space between particles is punctured as it is, and it becomes the porous membrane in which much puncturing was formed.

[0016] In this invention, condensation of a polymer particle is performed by destabilizing an emulsion. Although especially the method of destabilizing an emulsion and making a polymer particle condense is not limited, the sensible-heat gelling method and the optical gelling method are mentioned. How to give the property destabilized by the temperature change to the ** emulsion itself into the sensible-heat gelling method, For example, the approach and ** sensible-heat gelling agent which an emulsion is manufactured [gelling agent] using the Nonion system emulsifier with a cloudy point, and it warms [gelling agent] more than a cloudy point, and make an emulsion gel are added. There is the approach of making it gel by warming more than the setting temperature of this sensible-heat gelling agent etc., and when making the optical gelling method manufacture and gel an emulsion using a photodegradable emulsifier, irradiate light and an emulsifier is made to disassemble into it, and the approach of carrying out deactivation of the particle stabilization function is mentioned to it. In addition, the approach of manufacturing by performing an emulsion polymerization, and the approach of emulsion-izing by carrying out forcible distribution of the polymer into a water medium, after carrying out a polymerization with other polymerization methods shall be included in "manufacture" of an emulsion here.

[0017] There are an approach of giving sensible-heat gelation nature to the ** emulsion itself, and the approach of adding ** sensible-heat gelling agent as sensible-heat gelation approach as mentioned above. ** In order to adopt, after carrying out an emulsion polymerization using the Nonion system emulsifier which has a cloudy point or manufacturing a polymer independently, it is good to use the approach of making it distributing compulsorily using the Nonion system emulsifier (dispersant), and manufacturing an emulsion.

[0018] As an example of the Nonion system emulsifier, polyvinyl alcohol, denaturation polyvinyl alcohol, a fatty acid and polyethylene glycol ester, higher-alcohol polyethylene glycol ether, alkylphenol polyethylene glycol ether, an alkylamine polyethylene-glycol condensate, an alkylamide polyethylene-glycol condensate, a sorbitan fatty-acid-monoester polyethylene-glycol condensate, etc. are mentioned. These emulsifiers have a cloudy point 100 degrees C or more from 30-degree-C order according to a class. Control of scattering of water is easy, when a cloudy point makes an emulsifier 98 degrees C or less gel, since it is easy to obtain the porous membrane in which uniform puncturing was formed, it can be used preferably, but since a cloudy

point can be lowered by adding the water-soluble matter even if it is the emulsifier which has a cloudy point 100 degrees C or more, it can use.

[0019] The sensible-heat gelling agent which can be used by the approach ** Silicofluorides, such as a sodium silicofluoride and potassium silicofluoride, Metal complexes, such as an ammonium-sulfate zinc complex and an ammonium-carbonate zinc complex, A zinc oxide, inorganic or organic ammonium salt (these complexes), nitroparaffin, Organic ester, polyvinyl methyl ether, a polypropylene glycol, A polyether poly formal, a polyether denaturation polysiloxane, the alkylene oxide addition product of an alkylphenol formalin condensate, A functionality polysiloxane, water-soluble denaturation silicon oil, a silicone glycol copolymer, The Nonion system emulsifier which has a water-soluble polyamide, starch, methyl cellulose, hydroxyethyl cellulose, a carboxymethyl cellulose, protein, polyphosphoric acid, or the above-mentioned cloudy point is mentioned, and these one sort or two sorts or more can be mixed and used. Since it becomes that it is [control of setting temperature] easier to mix two or more sorts and to use a sensible-heat gelling agent, it is desirable, and nitroparaffin and organic ester have the effective concomitant use with a zinc oxide.

[0020] The desirable setting temperature of a sensible-heat gelling agent is 10-98 degrees C. Since the preservation stability after mixing an emulsion and a sensible-heat gelling agent, and pot life are not securable in setting temperature lower than 10 degrees C, it is not desirable. Moreover, in the case of the setting temperature exceeding 98 degrees C, since it is hard to obtain the porous membrane in which uniform puncturing was formed by the scattering rate of water becoming large rather than the gelation reaction, it is not desirable. In addition, a "sensible-heat gelation" operation of the semantics of the wide sense that progress of a gelation reaction is promoted remarkably shall be said by warming "sensible-heat gelation" not more than the semantics that gelation does not progress at all in ordinary temperature but more than setting temperature.

[0021] Rubber system latexes which made the subject an acrylic acid (meta) and its ester, and copolymerized one various organic functions and the polyfunctional monomer in which a polymerization is possible when the example was shown, although the presentation of an emulsion itself was not especially limited when the sensible-heat gelling method, the optical gelling method, and any were used, such as acrylic emulsion; SBR, and NBR, IR, NR; the thing which made polyester and polyurethane form into moisture powder is mentioned. Moreover, the blend of two or more sorts of emulsions may also be possible, and you may be the emulsion which has the particle of a core shell mold. Also when using especially the porous membrane of this invention for a recorded material, and a recorded agent is saved on ordinary temperature level, the activity of the emulsion of a configuration so that porosity may not be lost is recommended. That is, it is desirable to choose the emulsion of a configuration of to have controlled the mobility (deformability) even if Tg is lower, after coat-izing according to bridge formation, using the emulsion of a presentation of Tg of 0 degrees C or more.

[0022] As for the magnitude and transparency of puncturing of porous membrane which are acquired, it is desirable that the mean particle diameter of the polymer particle in an emulsion (polymer particle before condensing) uses a thing 10 micrometers or less in order to receive effect in the magnitude of the polymer particle in an emulsion. When using the emulsion of a polymer particle with a mean particle diameter of 10 micrometers or less, as for the porous membrane obtained, much detailed and uniform puncturing with an average diameter of 500nm or less was formed. Although the transparency of the porous membrane obtained receives effect also in the refractive index of a particle in addition to particle size, good transparency is acquired even if its refractive index is low compared with a non-subtlety particle since the porous membrane of this invention uses the polymer particle, and it does not make particle size extremely small.

[0023] An emulsion is destabilized and how to make a polymer particle condense is explained below. The layer of an emulsion [that water has been included] is fundamentally formed on a base material. Heat more than sensible-heat setting temperature, or an optical exposure (in the case of the optical gelation approach) is performed. If destabilize an emulsion, and it is made to condense, maintaining the particle condition of a polymer particle mostly (gelation) and water is

dispersed being simultaneous or subsequently with gelation before all the water in an emulsion layer disperses, the porous membrane of this invention can be obtained.

[0024] In a sensible-heat gelation system, if a gelation rate uses a sensible-heat gelling agent with low setting temperature quickly, even if scattering of the water from an emulsion layer takes place [be / it / under / gelation reaction progress / concurrency], uniform porous membrane will be obtained. What is necessary is on the other hand, just to disperse the water of an emulsion layer by the optical gelation approach, after performing an optical exposure at low temperature and making a polymer particle condense.

[0025] As for an emulsion, it is desirable to **** the nonvolatile matter to 20% of the weight or more. If lower than 20 % of the weight, since the absolute number of the polymer particle in an emulsion will decrease, while being hard coming to condense polymer particles, the crack by drying shrinkage etc. tends to go into a coat, and it is hard to obtain uniform porous membrane. Although especially the upper limit of a nonvolatile matter is not limited, since the number of the holes of the film obtained will decrease if it exceeds 70 % of the weight, or it becomes hyperviscosity by the magnitude of a hole turning small up, it is desirable that the problem of being bad also has the workability when carrying out coating, and it carries out to 70 or less % of the weight.

[0026] in order that [which explained the porous membrane of this invention until now] it may condense and gel and the polymer particle in an emulsion may coat-ize like, maintaining the particle condition mostly -- abbreviation -- the opening between spherical particles serves as special porous membrane which exists in a coat as puncturing. And if particle size distribution of a polymer particle is made into Sharp in order to use the gap of a particle as puncturing, the distribution degree of the diameter of puncturing can be made into Sharp. Moreover, if the magnitude and concentration of a polymer particle in an emulsion are controlled, it is possible to control freely the magnitude and the consistency (the number of puncturing per unit volume) of puncturing. By furthermore choosing a polymer presentation suitably according to an application, the porous membrane of this invention is applicable to various fields.

[0027] Since especially the porous membrane of this invention has the homogeneity of puncturing, and good transparency, the ink acceptance layer excellent in a water resisting property, transparency, color enhancement, and printing clear nature can be formed. For this reason, moreover, a highly efficient thing can be conventionally offered as a recorded material for ink jet recording methods compared with elegance that it is easy to deal with it. As an example of a recorded material, the recorded material which prepared the porous membrane of this invention is mentioned to transparent films, such as polystyrene including the OHP sheet in which the porous membrane of this invention was formed on the polyethylene terephthalate film (there may be an inclusion layer), polyethylene, polypropylene, polysulfone, and a polycarbonate. Moreover, although the porous membrane of this invention is proud of good transparency, since it shows fixable [which were excellent as an ink acceptance layer / the color enhancement or fixable] even if it prepares it in front faces, such as paper with an opaque base material, and a synthetic paper, it may be used for the recorded material for thermal ink transfer printing, a thermographic recording paper, etc.

[0028] Moreover, with an original raw material, if printing and printing prepare the porous membrane of this invention in front faces, such as ceramic products, such as difficult or impossible textiles, a plastic part, or earthenware, it can print to high degree of accuracy also to these raw materials.

[0029] Furthermore, since the porous membrane of this invention can also control the magnitude of puncturing by controlling the magnitude of the polymer particle in an emulsion, it is useful also in the special film related field which has an air filter, a filtration membrane and semipermeable membrane, and selective permeability in addition to the recorded material field mentioned above, and fields, such as a dc-battery separator.

[0030]

[Example] Although this invention is further explained in full detail according to an example below, the following example does not restrict this invention and all the things done for modification implementation in the range which does not deviate from before and the after-

mentioned meaning are included by the technical range of this invention. In addition, that it is especially with "%" and the "section" in the following examples shall express "% of the weight" and the "weight section", unless it refuses.

[0031] the flask equipped with example 1 dropping funnel, an agitator, nitrogen installation tubing, the thermometer, and the reflux condenser -- the ion-exchange-water 170 section and NONIPORU 200 (polyethylene-glycol nonylphenyl ether system emulsifier by Sanyo Chemical Industries, Ltd.) -- the 17 sections and new pole PE-64 (polyethylene-glycol-polypropylene-glycol block-copolymer system emulsifier by Sanyo Chemical Industries, Ltd.) -- 2 section preparation -- it heated at 45 degrees C, blowing nitrogen gently. The monomer mixture which consists of the methyl-methacrylate 292 section, the butyl acrylate 23 section, and the styrene 135 section was put into the dropping funnel, and 25% of them was dropped in the flask.

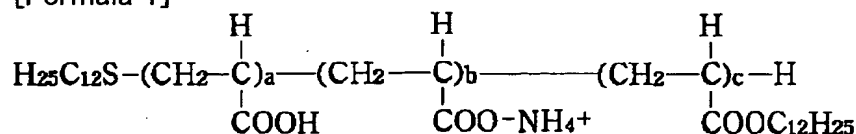
[0032] Then, the 15 sections and the 3% water-solution 15 section of ammonium persulfate were added for 1% water solution of a sodium hydrogensulfite in the flask. The 1% water-solution 62 of the remaining monomer mixture and a sodium hydrogensulfite section and the 1% water-solution 62 section of ammonium persulfate were dropped for 3 hours after 30 minutes, respectively. During dropping, the temperature in a flask was held at 50-54 degrees C, it agitated at this temperature after dropping termination further for 1 hour, and the polymerization was terminated. The aqueosity resin dispersant [1] which the polymer particle with 50.2% of nonvolatile matters, a pH [2.1], and a mean particle diameter of 120nm distributed was obtained.

[0033] In this aqueosity resin dispersant [1] 100 section, the aqueous ammonia 108 section, in addition produced 48% water solution of ammonium-sulfate zinc complexes were beforehand agitated well 6 ****s 25% to the zinc-sulfate 100 section, and the emulsion for spreading [1] was obtained in it. the 100-micrometer PET film with which 3-micrometer polyvinyl alcohol is applied as a primer layer -- the bar coating machine of #20 -- using -- the emulsion for spreading [1] -- coating -- carrying out -- immediately -- the constant temperature of 80 degrees C and 60% of humidity -- it put into a constant humidity in a plane for 15 minutes, and gelation of the polymer particle in an emulsion layer and desiccation of a coat were performed. The OHP sheet for ink jet record [1] with which the ink acceptance layer whose desiccation thickness is 25 micrometers was formed was obtained.

[0034] It heated at 80 degrees C, having taught the ion-exchange-water 322 section to the flask equipped with example 2 dropping funnel, an agitator, nitrogen installation tubing, the thermometer, and the reflux condenser, and blowing nitrogen into it gently. Churning mixing of the methyl-methacrylate 265 section, the divinylbenzene 117 section, the gamma-methacryloxypropyl-trimethoxy-silane 8 section, the 20% water-solution 70 section of the emulsifier represented with the following type, the ion-exchange-water 175 section, and the 25% aqueous ammonia 3 section was carried out, the pre emulsion for dropping was prepared, and 2% of them was dropped at the flask.

[0035]

[Formula 1]



[0036] (However, as an average of an emulsifier, the sum total of a and b is 20 and c is 1 or 2.) Moreover, each monomer unit shall be combined at random by the intramolecular of an emulsifier.

Then, the 5% water-solution 20 of potassium persulfate section was poured into the flask, dropping of the remaining pre emulsions was started after 30 minutes, and dropping was ended 5 hours after. During dropping, the temperature in a flask was held at 78-82 degrees C, 20 section addition charge of the 2% water solution of potassium persulfate was carried out after dropping termination, it agitated at this temperature further for 1 hour, the polymerization was terminated, and the aqueosity resin dispersant [2] which the polymer particle with 40.4% of nonvolatile matters, a pH [8.1], and a mean particle diameter of 176nm distributed was obtained.

[0037] TPA-4380 (Toshiba Silicone polyether denaturation silicone system sensible-heat gelling agent) was well agitated for 48% water solution of ammonium-sulfate zinc complexes produced like the example 1 in this aqueosity resin dispersant [2] 100 section 1 ***** with the 7.5 sections, and the emulsion for spreading [2] was obtained. # Except having used the bar coating machine of 26, like the example 1, coating and gelation, and when it dried, the OHP sheet [2] which has the ink acceptance layer of 25 micrometers of desiccation thickness was obtained in the emulsion for spreading [2].

[0038] It heated at 70 degrees C, having taught the ion-exchange-water 183 section and the Aqualon HS-10 (reactant emulsifier of Dai-Ichi Kogyo Seiyaku nature) 1 section to the flask equipped with example 3 dropping funnel, an agitator, nitrogen installation tubing, the thermometer, and the reflux condenser, and blowing nitrogen into it gently. Mixed churning of the seven sections and the ion-exchange-water 194 section was carried out for Aqualon HS-10 with the methyl-methacrylate 298 section, the 2-ethylhexyl acrylate 141 section, the styrene 50 section, the acrylic-acid 6 section, and the glycidyl methacrylate 5 section, the pre emulsion for dropping was prepared, and 5% of them was dropped in the flask.

[0039] Then, the 20 sections and the 3% water-solution 20 section of potassium persulfate were added for 1% water solution of a sodium hydrogensulfite in the flask. The 1% water-solution 37 of the remaining pre emulsions and a sodium hydrogensulfite section and the 3% water-solution 37 section of potassium persulfate were dropped for 3 hours after 15 minutes, respectively. During dropping, the temperature in a flask was held at 68-72 degrees C, it agitated at this temperature after dropping termination further for 1 hour, and the polymerization was terminated. The aqueosity resin dispersant [3] which the polymer particle with 50.9% of nonvolatile matters, a pH [1.7], and a mean particle diameter of 118nm distributed was obtained.

[0040] Beforehand, in this aqueosity resin dispersant [3] 100 section, 45% water solution of ammonium-carbonate zinc complexes which added the zinc-oxide 46 section, the ammonium-hydrogencarbonate 49 section, and the 25% aqueous ammonia 116 section, and was made was agitated well 10 *****, and the emulsion for spreading [3] was obtained in it. 3-micrometer polyvinyl alcohol used the bar coating machine of #20 for the 100-micrometer PET film applied as a primer layer, and carried out coating of the emulsion for spreading [3] to it. immediately -- the constant temperature of 80 degrees C and 96% of humidity -- put into a constant humidity in a plane for 1 minute, subsequently to the inside of a 80-degree C dryer put in, it was made to dry for 1 minute, and gelation of the polymer particle in an emulsion layer and desiccation of a coat were performed. The OHP sheet [3] with which the ink acceptance layer whose desiccation thickness is 25 micrometers was formed was obtained.

[0041] It heated at 70 degrees C, having taught the ion-exchange-water 275 section to the flask equipped with example 4 dropping funnel, an agitator, nitrogen installation tubing, the thermometer, and the reflux condenser, and blowing nitrogen into it gently. Mixed churning of the butyl acrylate 315 section, the divinylbenzene 135 section, and the high tenor N-08 (Dai-Ichi Kogyo Seiyaku polyethylene-glycol. alkylphenyl ethereal sulfate ammonium) 16 section that are the 27 sections and an anion system emulsifier about NONIPORU 200 (emulsifier of the Sanyo Chemical Industries polyethylene-glycol nonylphenyl ether system) was carried out with the ion-exchange-water 214 section, the pre emulsion for dropping was prepared, and 5% of them was dropped in the flask.

[0042] Subsequently, the five sections were added for 5% water solution of 2 and 2'-azobis (2-amidinopropane) dihydrochloride in the flask. The remaining pre emulsions were dropped for 3 hours after 20 minutes. During dropping, the temperature in a flask was held at 68-72 degrees C, it agitated at this temperature after dropping termination further for 1 hour, and the polymerization was terminated. The aqueosity resin dispersant [4] which the polymer particle with 49.8% of nonvolatile matters, a pH [1.8], and a mean particle diameter of 132nm distributed was obtained.

[0043] 48% water solution of ammonium-sulfate zinc complexes produced like the example 1 in this aqueosity resin dispersant [4] 100 section was agitated well 10 *****, the emulsion for spreading [4] was produced, and the OHP sheet [4] with which the ink acceptance layer whose desiccation thickness is 25 micrometers was formed like the example 1 was obtained.

[0044] It heated at 80 degrees C, having taught the 20% water-solution 80 of the emulsifier used in the ion-exchange-water 223 section and the example 2 section, and the 25% aqueous ammonia 3 section to the flask equipped with example 5 dropping funnel, an agitator, nitrogen installation tubing, the thermometer, and the reflux condenser, and blowing nitrogen into it gently. Churning mixing of the methyl-methacrylate 324 section, the divinylbenzene 36 section, the 20% water-solution 36 section of the emulsifier used in the example 2, and the 25% aqueous ammonia 2 section and the ion-exchange-water 142 section was carried out, the pre emulsion for dropping was prepared, and 15% of them was dropped at the flask.

[0045] Then, the 1% water-solution 10 of a sodium hydrogensulfite section and the 5% water-solution 24 section of potassium persulfate were added in the flask. Dropping of remaining pre EMARUSHO was begun after 30 minutes, and dropping was ended over 4 hours. During dropping, the temperature in a flask was held at 78-82 degrees C, and 20 section addition charge of the potassium persulfate water solution was carried out 2% 2 hours after dropping initiation. Furthermore, after dropping termination, 20 sections of 2% of potassium persulfate water solutions were thrown in, and they were agitated for 3 hours.

[0046] Next, it was dropped in the flask, having pre applied [which agitated the 20% water-solution 4 of the emulsifier used in the ethyl-acrylate 30 section, the N-vinyl-pyrrolidone 8 section, the glycidyl methacrylate 2 section, and the example 2 section, and the ion-exchange-water 16 section, and was prepared] it for 30 minutes. During dropping, the temperature in a flask was held at 68-72 degrees C, the 20 sections of 2% water solutions of potassium persulfate were thrown in after dropping termination, it agitated at this temperature further for 1 hour, and the polymerization was terminated. The aquosity resin dispersant [5] which the polymer particle with 42.3% of nonvolatile matters, a pH [8.0], and a mean particle diameter of 50nm distributed was obtained.

[0047] In this aquosity resin dispersant [5] 100 section, TPA-4390 (Toshiba Silicone polyether denaturation silicone system sensible-heat gelling agent) was agitated well 3 *****, the emulsion for spreading [5] was produced, and the OHP sheet [5] which has the ink acceptance layer of 25 micrometers of desiccation thickness was obtained like the example 2.

[0048] the flask equipped with example 6 dropping funnel, an agitator, nitrogen installation tubing, the thermometer, and the reflux condenser -- the ion-exchange-water 183 section and Aqualon HS-10 -- 1 section preparation -- it heated at 70 degrees C, blowing nitrogen gently. Mixed churning of the seven sections and the ion-exchange-water 194 section was carried out for Aqualon HS-10 with the methyl-methacrylate 155 section, the 2-ethylhexyl acrylate 284 section, the styrene 50 section, the acrylic-acid 6 section, and the glycidyl methacrylate 5 section, the pre emulsion for dropping was prepared, and 5% of them was dropped in the flask.

[0049] Then, the 20 sections and the 3% water-solution 20 section of potassium persulfate were added for 1% water solution of a sodium hydrogensulfite in the flask. The 1% water-solution 37 of the remaining pre emulsions and a sodium hydrogensulfite section and the 3% water-solution 37 section of potassium persulfate were dropped for 3 hours after 15 minutes, respectively. During dropping, the temperature in a flask was held at 68-72 degrees C, it agitated at this temperature after dropping termination further for 1 hour, and the polymerization was terminated. The aquosity resin dispersant [6] which the polymer particle with 50.6% of nonvolatile matters, a pH [1.8], and a mean particle diameter of 128nm distributed was obtained.

[0050] The these aquosity resin dispersant [6] 10 section and the aquosity resin dispersant [2] 90 section obtained in the example 2 were added, 48% water solution of TPA-ammonium-sulfate zinc complexes which produced 4380 (Toshiba Silicone polyether denaturation silicone system sensible-heat gelling agent) like the one section and an example 1 was agitated well 5 *****, and the emulsion for spreading [6] was obtained. the 100-micrometer PET film with which 3-micrometer polyvinyl alcohol is applied as a primer layer -- the bar coating machine of #24 -- using -- the emulsion for spreading [4] -- coating -- carrying out -- immediately -- the constant temperature of 80 degrees C and 96% of humidity -- after putting into a constant humidity in a plane for 1 minute and making it gel, it was made to dry within 80-degree C hot air drying equipment for 1 minute, and the OHP sheet [6] with which the ink acceptance layer whose desiccation thickness is 25 micrometers be formed be produced.

[0051] To the aqueous resin dispersant [1] 87 section obtained in the example 7 example 1, it is 2, 2, and 4-trimethyl. The 1 and 3-pentanediol monochrome iso butyrate 13 section was added, and it agitated well. 48% water solution of ammonium-sulfate zinc complexes produced like the example 1 to this aqueous resin dispersant was agitated well 5 *****, and the emulsion for spreading [7] was obtained. the 100-micrometer PET film with which 3-micrometer polyvinyl alcohol is applied as a primer layer -- the bar coating machine of #26 -- using -- the emulsion for spreading [7] -- coating -- carrying out -- immediately -- the constant temperature of 80 degrees C and 96% of humidity -- after putting into a constant humidity in a plane for 1 minute and making it gel, it was made to dry within 80-degree C hot air drying equipment for 1 minute, and the OHP sheet [7] with which the ink acceptance layer whose desiccation thickness is 25 micrometers be formed be produced.

[0052] Using the aqueous resin dispersant [3] obtained in the example of comparison 1 example 3 as an emulsion for spreading [8] as it is, it applied to the 100-micrometer PET film with which 3-micrometer polyvinyl alcohol is applied as a primer layer by the bar coating machine of #30, and dried for 1 minute with 80-degree C hot air drying equipment. The OHP sheet for a comparison [8] with which the ink acceptance layer whose desiccation thickness is 25 micrometers was formed was produced.

[0053] Coating of the 10% water solution of example of comparison 2 PVA-CST (Kuraray polyvinyl alcohol) was carried out to the 100-micrometer PET film so that it might become 25 micrometers of desiccation thickness, and it dried for 15 minutes using the 80-degree C dryer, and the OHP sheet for a comparison [9] with which the PVA system ink acceptance layer was formed was produced.

[0054] after add the 10-% water solution 20 of above-mentioned PVA-CST section in the example of comparison 3 Snow tex C(colloidal silica made from Nissan chemistry: particle size of 20-40nm) 100 section and agitate in it, coating be carried out to the 100-micrometer PET film, it dried for 15 minutes using the 80-degree C dryer, and the OHP sheet for a comparison [10] with which the PVA system ink acceptance layer be formed be produced so that it might become 25 micrometers of desiccation thickness.

[0055] 45% water solution of ammonium-carbonate zinc complexes produced like the example 3 in the aqueous resin dispersant [6] 100 section obtained in the example of reference 1 example 6 was agitated well 10 *****, and the emulsion for spreading [11] was obtained. the 100-micrometer PET film with which 3-micrometer polyvinyl alcohol is applied as a primer layer -- the bar coating machine of #28 -- using -- the emulsion for spreading [11] -- coating -- carrying out -- immediately -- the constant temperature of 80 degrees C and 96% of humidity -- after putting into a constant humidity in a plane for 1 minute and making it gel, it was made to dry within 80-degree C hot air drying equipment for 1 minute, and the OHP sheet [11] with which the ink acceptance layer whose desiccation thickness is 25 micrometers be formed be produced.

[0056] About OHP sheet [1]- [11] obtained in the performance-evaluation approach examples 1-7, the examples 1-3 of a comparison, and the example 1 of reference, the color pattern was printed using ink jet printer MJ-5000C made from EPSON, the following approaches estimated drying [of the ink], color enhancement, the repeatability of a dot, a water resisting property, transparency, and a surface state, and the result was shown in a table 1.

[0057] After often rubbing a copy paper with a finger from on superposition into a printing part immediately after [drying] color pattern printing, it observed visually how many printing patterns were imprinted by the copy paper. The valuation basis is as follows.

O : -- completely -- not imprinting -- *: -- x: imprinted slightly -- [0058] imprinted considerably when the printing section of an OHP sheet is directly viewed by making into a criterion what printed the [color-enhancing] color pattern on the paper only for ink jets (it abbreviates to "accepting reality" in a table), and when it projects on a screen using an OHP projector (it abbreviates to "projection" in a table), or it is coloring finely compared with a reference standard (is the color reproduced?) -- or [how] -- ***** -- the following criteria estimated.

O :color-enhancing fitness *: poor x:coloring [0059] an amorous glance is a little different from

The pattern printed on the [dot repeatability] sheet was expanded and observed with the magnifier, and the following criteria estimated the configuration of a dot.

O : — **: which is carrying out the beautiful round shape — x: which is deforming slightly — [0060] which is deforming considerably Several drops of water was hung down to the [waterproof] printing side, and the following criteria estimated the condition of the ink acceptance layer when rubbing 10 times with a finger.

O : — change-less **: [0061] into which the whole x:ink acceptance layer into which ink begins to melt slightly begins to melt It projected with the projector whether there would be any transparency usable as a [transparency] OHP sheet, and the following criteria estimated it.

O : — transparency — problem-less **: — [0062] to which x:projection image on which a projection image wears the yellow taste slightly becomes quite dark The front face of a [surface state] OHP sheet was expanded by 20,000 times using the scanning electron microscope (SEM), and the formation condition of a hole was observed. Moreover, the SEM photograph of the welding condition of the particle of examples 1 and 3 and the example 1 of a comparison was shown in drawing 2 -4. In the example 1, it turns out that the pattern B in drawing 1 and the example 3 serve as a homogeneity coat of Pattern A in the example 1 of a comparison by obtaining the thing near Pattern C.

[0063]

[A table 1]

OHPシート トNo.		乾燥性	発色性		ドット 再現性	耐水性	透明性	表面状態	備 考
			直視	投影					
実 施 例	[1]	○	○	○	○	○	○	多 孔 質	計算T _g 90℃
	[2]	○	○	△	○	○	○～△	多 孔 質	高T _g モノマー架橋
	[3]	○	○	○	○	○	○	多 孔 質	計算T _g 30℃
	[4]	○	○	△	○	○	○～△	多 孔 質	低T _g モノマー架橋
	[5]	○	○	○	○	○	○	多 孔 質	コア・シェルタイプ
	[6]	○	○	○	○	○	○～△	多 孔 質	2種類ブレンド系
	[7]	○	○	○	○	○	○	多 孔 質	成膜助剤使用
比 較 例	[8]	×	△	×	×	△	○	無孔	通常乾燥
	[9]	△	○	○	○～△	×	○	無孔	PVA
	[10]	○	×	×	○	×	×	多 孔 質	シリカ粒子+PVA
参考例[11]		×	△	×	×	△	○	孔 少 量	計算T _g -20℃

[0064]

[Effect of the Invention] The porous membrane of this invention makes the polymer particle in an emulsion condense maintaining the particle condition mostly, and makes much micropores by the gap of particles form by coat-izing. For this reason, the magnitude of puncturing of porous membrane, hole density, the consistency of a hole, etc. can be broadly changed freely by controlling the magnitude of the polymer particle in an emulsion, and particle size distribution or the solid content concentration of an emulsion. The porous membrane of this invention is utilizable for other recorded materials including the recorded material for [which can utilize the homogeneity of puncturing, and good transparency] ink jet recording methods, and various applications, such as the film field.